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(71) Applicant: BP Chemicals Limited  
Belgrave House 76 Buckingham Palace Road  
London, SW1W 0SU(GB)

(72) Inventor: Cameron, Robert  
BP Chemicals Limited Chertsey Road  
Sunbury-on-Thames Middlesex, TW16 7LN(GB)

(74) Representative: Harry, John et al,  
BP INTERNATIONAL LIMITED Patents and Licensing  
Division Chertsey Road  
Sunbury-on-Thames Middlesex TW16 7LN(GB)

(54) Dismutation of functionalised olefins.

(57) The present invention is a method for the (co)dismutation of a feedstock comprising functional olefins. The feedstock, which has at least one terminally unsaturated ester, is dismutated using a hybrid metathesis catalyst composition which has a tungsten halide and an organometallic compound of the formula  $R_3R^1M$  wherein,  $R^1$  is a group selected from an alkyl and an aryl group,  $R$  is a group selected from  $R^1$  and a hydrogen atom, and  $M$  is a metal atom capable of exhibiting more than one oxidation state, on a support.

The activity of this heterogeneous catalyst composition for dismuting terminally unsaturated ester is vastly superior to the corresponding homogeneous systems.

DISMUTATION OF FUNCTIONALISED OLEFINS

The present invention relates to (co)dismutation of functionalised terminal olefins using a hybrid metathesis catalyst composition.

5 Dismutation of internal olefins by hybrid tungsten-based metathesis catalysts is known. A paper by Mol,J.C. et al entitled, "Hybrid Tungsten-Based Metathesis Catalysts" in the Journal of Molecular Catalysis, 8 (1980), 185-190 discloses that homogeneous catalyst systems are better for dismuting internal olefinic compounds than the hybrid heterogeneous systems and this relative lack of  
10 activity of heterogeneous systems is said to be even more pronounced in the case of unsaturated esters such as methyl oleate.

It has now been found that the activity of heterogeneous catalyst compositions for dismuting unsaturated esters which are terminally unsaturated is vastly superior to the corresponding homogeneous  
15 systems.

Accordingly, the present invention is a method for the dismutation of a feedstock comprising at least one terminally unsaturated ester using a hybrid metathesis catalyst composition which comprises a tungsten halide and an organo-metallic compound of  
20 the formula  $R_3R^1M$  wherein,  $R^1$  is a group selected from an alkyl and an aryl group, R is a group selected from  $R^1$  and a hydrogen atom, and M is a metal atom capable of exhibiting more than one oxidation state, on a support.

The term "dismutation" as used herein and throughout the  
25 specification is meant to include both self-dismutation and

codismutation with other unsaturated esters.

In the hybrid metathesis catalyst composition the tungsten halide is preferably tungsten hexa-halide, most preferably tungsten hexa-chloride.

5       The organo-metallic compound is preferably selected from a monohydrotrialkyl-, a tetraalkyl-, a monohydrotriaryl- and a tetraaryl-derivative of the metal. The metal atom M is suitably selected from those in Groups IIB, IIIA and IVA of the Periodic Table of Elements in the 44th Edition of the "Handbook of Chemistry and  
10       Physics", Ed. Hodgman, C.D. et al, pp 448 and 449 (1963) and published by The Chemical Rubber Publishing Co., Ohio, U.S.A. The metal is preferably selected from zinc, mercury, aluminium, tin, germanium and lead. The organo-metallic compound is most preferably tetra-methyl-tin.

15       The support used is preferably silica.

The hybrid metathesis catalyst may be prepared by conventional techniques. For instance, a suspension of tungsten hexachloride and the support eg silica in a solvent such as dichloroethane may be refluxed, allowed to cool, separated from the supernatant liquid and  
20       washed repeatedly with the solvent. The resultant tungsten hexachloride-silica catalyst for instance is deep red in colour.

The terminally unsaturated ester is suitably a monoester and preferably one in which the terminal unsaturation is remote from the functional carboxyl group. The ester may be derived from an  
25       unsaturated carboxylic acid which has at least 4 carbon atoms, preferably between 5 and 30 carbon atoms.

The terminally unsaturated esters may be codismuted with internally unsaturated esters to produce the corresponding products. Specific examples of internally unsaturated esters which may be  
30       codismuted include methyl hex-3-enoate and ethyl pent-3-enoate.

The dismutation reaction is suitably carried out by contacting the unsaturated ester with the hybrid metathesis catalyst composition at elevated temperature, preferably by refluxing the reactant ester in a solvent such as a chlorinated hydrocarbon in the presence of the  
35       catalyst. The dismutation products are then separated and recovered by conventional techniques.

The process of the present invention together with the relevant Comparative Tests are described below.

#### Examples and Comparative Tests

##### Preparation of Catalyst

5 The materials used were as follows pretreated as indicated.

Silica gel (Davison Grace 952, B.E.T. surface area  $330 \text{ cm}^2\text{g}^{-1}$ ) was activated by heating for 24 hours at 823K in flowing nitrogen and stored under nitrogen.  $\text{WCl}_6$  was used as supplied (Koch Light). Tetramethyltin (Aldrich) and Nonane (Aldrich) were dried over  
10 activated molecular sieves ( $3 \text{ \AA} + 4 \text{ \AA}$ ). Dichloroethane was refluxed over activated molecular sieves ( $3 \text{ \AA} + 4 \text{ \AA}$ ) and distilled before use. Methyl pentenoate and undecylenoate were prepared from the corresponding acids and distilled before use. All reactions were carried out in dried glassware under nitrogen.

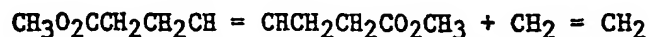
15 To  $\text{WCl}_6$  (0.4g,  $1 \times 10^{-3} \text{ mol}$ ) dissolved in dichloroethane (20ml) was added Silica gel (4g) (Davison Grace 952). The dark blue suspension was allowed to stand, with occasional stirring for eighteen hours. The supernatant liquid was decolourised after a period of several hours. The resulting suspension was refluxed for 10 minutes,  
20 allowed to cool, the supernatant liquid removed and the solid washed repeatedly with dichloroethane ( $3 \times 20\text{ml}$ ). The  $\text{WCl}_6 - \text{SiO}_2$  catalyst so formed was deep red in colour.

Analysis of the catalyst showed a W content of 4% wt/wt representing a loading of 0.08g  $\text{WCl}_6$  per g silica.

##### 25 Examples 1 - 3

##### Metathesis of Methyl pent-4-enoate

$2(\text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{CO}_2\text{CH}_3)$  in equilibrium with



General procedure for hybrid reaction:-

30 To a suspension of  $\text{WCl}_6$  on silica in dichloroethane was added nonane, tetramethyltin and methylpentenoate. The resulting suspension was then refluxed at atmospheric pressure and  $80^\circ\text{C}$ , the supernatant remaining clear throughout, while the solid becomes dark blue.

Results

|   | <u>WCl<sub>6</sub> : Me<sub>4</sub>Sn : Ester</u> | <u>% Yield</u> |
|---|---|----------------|
|   | 1 : 2 : 70  | 85             |
|   | 1 : 2 : 120                                       | 75             |
| 5 | 1 : 2 : 260                                       | 29             |

Comparative Tests (not according to the invention)

General procedure for homogeneous reaction:

To a solution of WCl<sub>6</sub> in dichloroethane was added, nonane (internal standard), tetramethyl tin (co-catalyst) and methyl  
 10 pentenoate. The resulting dark blue solution was then refluxed as before.

Results

|    | <u>WCl<sub>6</sub> : Me<sub>4</sub> Sn : Ester</u> | <u>% Yield</u> |
|----|--|----------------|
|    | (i) 1 : 2 : 75                                     | 38             |
| 15 | (ii) 1 : 2 : 290                                   | 21             |

Example 4Metathesis of Methyl Undecyl-10-enoate

2 (CH<sub>2</sub> = CH (CH<sub>2</sub>)<sub>8</sub> - CO<sub>2</sub>CH<sub>3</sub>) in equilibrium with  
 CH<sub>3</sub>O<sub>2</sub>C(CH<sub>2</sub>)<sub>8</sub>CH = CH (CH<sub>2</sub>)<sub>8</sub> - CO<sub>2</sub>CH<sub>3</sub> + CH<sub>2</sub> = CH<sub>2</sub>

20 The reaction conditions and procedures were as described under Examples 1-3 above.

Results

|    | <u>Catalyst</u>  | <u>% Conversion</u><br><u>after 1 hour</u> | <u>% Conversion</u><br><u>after 6 hours</u> |
|----|--|--|---|
| 25 | WCl <sub>6</sub> /SiO <sub>2</sub> /Me <sub>4</sub> Sn | 79   | 96  |

In all cases WCl<sub>6</sub> : Me<sub>4</sub>Sn : Ester = 1 : 2 : 25

Comparatives Test (iii)

The procedure of Examples 4 was repeated using a homogeneous catalyst system (without silica).

30 Results

|  | <u>Catalyst</u>                      | <u>% Conversion</u><br><u>after 1 hour</u> | <u>% Conversion</u><br><u>after 6 hours</u> |
|--|--------------------------------------|--|---|
|  | WCl <sub>6</sub> /Me <sub>4</sub> Sn | 65   | 80  |

Examples 5 and 6 and Comparative Tests (iv)-(ix)

These were carried out using different esters but using respectively the same procedure as in Examples 1-3 above and Comparative Tests (i) and (ii) above. The results are tabulated

5 below:

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TABLE I

| <u>Ester</u> |  | <u>Catalyst<sup>a</sup></u>                                | <u>Yield (%)<sup>c</sup></u> | <u>Products</u>  |
|--------------|--|--|------------------------------|--|
| (iv)         | C <sub>8</sub> -C=C-C <sub>7</sub> -COOC | WCl <sub>6</sub> /Me <sub>4</sub> Sn                       | 52 )                         | C <sub>8</sub> -C=C-C <sub>8</sub> + COOC-C <sub>7</sub> -C=C-C <sub>7</sub> -COOC |
| (v)          | "  | WCl <sub>6</sub> /SiO <sub>2</sub> /Me <sub>4</sub> Sn     | 2 )                          |  |
| (vi)         | C=C-C <sub>9</sub> -COOC                 | WCl <sub>6</sub> /Me <sub>4</sub> Sn                       | 72 )                         | C=C + COOC-C <sub>9</sub> -C=C-C <sub>9</sub> -COOC                                |
| 5            | "  | WCl <sub>6</sub> /SiO <sub>2</sub> /Me <sub>4</sub> Sn     | 96 )                         |  |
| (vii)        | C-C-C=C-C-C-COOC                         | WCl <sub>6</sub> /Me <sub>4</sub> Sn (b)                   | 38 )                         | C <sub>2</sub> -C=C-C <sub>2</sub> + COOC-C-C=C-C-C-COOC                           |
| (viii)       | "  | WCl <sub>6</sub> /SiO <sub>2</sub> /Me <sub>4</sub> Sn (b) | - )                          |  |
| (ix)         | C=C-C-C-C-COOC                           | WCl <sub>6</sub> /Me <sub>4</sub> Sn                       | 65 )                         | C=C + COOC-C-C=C-C-C-COOC  |
| 6            | "  | WCl <sub>6</sub> /SiO <sub>2</sub> /Me <sub>4</sub> Sn     | 80 )                         |  |

a) (ester)/(WCl<sub>6</sub>) = 25; (WCl<sub>6</sub>)/(Me<sub>4</sub>Sn) = 0.33; solvent: dichloroethaneb) (WCl<sub>6</sub>)/(Me<sub>4</sub>Sn) = 0.5

c) after six hours at 80°C

Claims:

1. A method for the (co)dismutation of a feedstock comprising at least one terminally unsaturated ester using a hybrid metathesis catalyst composition which comprises a tungsten halide and an organo-metallic compound of the formula  $R_3R^1M$  wherein,  $R^1$  is a group selected from an alkyl and an aryl group, R is a group selected from  $R^1$  and a hydrogen atom, and M is a metal atom capable of exhibiting more than one oxidation state, on a support.
2. A method according to claim 1 wherein the tungsten halide is a tungsten hexa-halide.
- 10 3. A method according to claim 1 wherein the organo-metallic compound is selected from a monohydrotrialkyl-, a tetraalkyl-, a monohydrotriaryl- and a tetraaryl-derivative of the metal.
4. A method according to claim 1 wherein the metal atom M is selected from those in Groups IIB, IIIA and IVA of the Periodic Table of Elements as herein defined.
- 15 5. A method according to any one of the preceding claims wherein the metal is selected from zinc, mercury, aluminium, tin, germanium and lead.
6. A method according to any one of the preceding claims wherein the organo-metallic compound is tetra-methyl-tin.
- 20 7. A method according to any one of the preceding claims wherein the support used is silica.
8. A method according to any one of the preceding claims wherein the terminally unsaturated ester is a monoester.
- 25 9. A method according to claim 8 wherein the terminally unsaturated ester is one in which the terminal unsaturation is furthest from the functional carboxyl group.



10. A method according to any one of the preceding claims wherein the terminally unsaturated ester is codismuted with an internally unsaturated ester.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

0084437

Application number

EP 83 30 0162

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |  |   |
|---|---|--|---|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim                              | CLASSIFICATION OF THE APPLICATION (Int. Cl. *)  |
| A   | <p>FR-A-2 252 314 (JAPAN SYNTHETIC RUBBER CO.)</p> <p>*Page 1, line 36 - page 2, line 10; page 4, line 19 - page 5, line 25; page 7, line 9 - page 8, line 8; page 12; example 6*</p> | 1-6, 8-10                                      | <p>C 07 C 69/593</p> <p>C 07 C 67/475//</p> <p>B 01 J 27/08</p>                       |
| A   | <p>FR-A-2 389 588 (RHONE-POULENC)</p> <p>*Page 2, line 14 - page 3, line 40; pages 8-9; examples 4,5*</p>   | 1-6, 8-10                                      |   |
|   |   |  | <p>TECHNICAL FIELDS SEARCHED (Int. Cl. *)</p> <p>C 07 C 69/00</p> <p>C 07 C 67/00</p> |
| The present search report has been drawn up for all claims  |   |  |   |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>28-02-1983 | Examiner<br>KINZINGER J.M.  |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p> |   |  |   |